(12) UK Patent Application (19) GB (11) 2 205 329 (13) A

(43) Application published 7 Dec 1988

(21) Application No 8812348

(22) Date of filing 25 May 1988

(30) Priority data
(31) 86899 (32) 27 May 1987 (33) LU

(71) Applicant
L'Oreal

(Incorporated in France)

14 rue Royale, 75008 Paris, France

(72) Inventors
Jean-Francois Grollier
Didier Garoche
Jean Cotteret

(74) Agent and/or Address for Service
J A Kemp & Co
14 South Square, Gray's Inn, London, WC1R 5EU

(51) INT CL⁴
A61K 7/13

(52) Domestic classification (Edition J):
D1B 2A4

(56) Documents cited
GB A 2197885 GB A 2185498 GB A 2138845
GB A 2024873 GB A 2003938 GB 1569845
GB 1513672

(58) Field of search
D1B
Selected US specifications from IPC sub-class
A61K

(54) Dyeing keratinous fibres with oxidation dyes together with iodide ions

(57) Keratinous fibres, esp. human hair, are dyed by applying in either order:-
(a) a composition comprising an oxidation base and iodide ions, and optionally 5,6 – dihydroxyindole, but preferably no further reactant (coupler); and
(b) a composition comprising hydrogen peroxide.

The oxidation base may be of the *o* – or *p* – phenylenediamine, *o* – or *p* – aminophenol, N,N' – diphenylalkylenediamine or heterocyclic series. The iodide ions may be provided by an alkali metal, alkaline earth metal or ammonium iodide. Multicompartment kits for the compositions are disclosed.

Advantages of the process include, rapid wash - and light - fast colorations without the need for alkalinising agents.

GB 2 205 329 A

PROCESS FOR DYEING KERATINOUS FIBRES WITH OXIDATION BASES COMBINED WITH AN IODIDE AND DYEING COMPOSITION EMPLOYED

The present invention relates to a new process for the dyeing of keratinous fibres, especially human keratinous fibres such as hair, with oxidation bases, to the compositions employed in this process and to devices for dyeing.

For many years, either so-called "direct" dyes, capable in themselves of colouring keratinous fibres, or so-called "oxidation" dyes which, after the development of their dyeing power in an oxidizing medium, enable a coloration to be obtained which is resistant to several treatments with shampoo, to light and to inclement weather, have been used for the dyeing of keratinous fibres, and especially hair.

Oxidation dyes are generally not dyes in themselves; they are intermediate compounds initially having little or no colour, commonly referrred to as "oxidation bases or precursors", which develop their dyeing power in an oxidizing medium, generally consisting of hydrogen peroxide, to give rise in a basic medium to a dye in accordance with a process, either of oxidative condensation of the oxidation dye precursor with itself, or of an oxidative condensation of the "oxidation base or dye precursor" with a compound referred to as a "colour modifier" or "coupler".

The variety of molecules involved, formed by these different oxidation dyes and the possiblity of coupling them, makes it possible to obtain a rich palette of

colourings in respect of ashen, black, natural hues and hues with glints.

A coloration of this kind is referred to as a "permanent coloration", as opposed to the coloration obtained with the so-called "direct" dyes, which is a so-called "semi-permanent" coloration.

Processes employing a pretreatment with ions in the form of soluble salts, followed by the application of oxidation dyes after an intermediate rinsing stage, have already been proposed in the past.

The Applicant has discovered, and this forms the subject of the invention, a process using a composition containing, in combination, oxidation bases and an iodide ion, enabling hues to be obtained which can be different or stronger than those formerly obtained with the traditional system of oxidative polymerization of these bases with couplers.

He also found that the colorations thereby obtained made it possible to decrease the exposure times and, in this manner, to produce a dyeing much more rapidly than with the systems of the prior art.

This process also enables hair to be dyed with oxidation bases in an acidic medium and without employing the alkalinizing agents traditionally used in the field of oxidation dyeing, such as ammonia solution and amines, which impart an undesirable odour to the compositions employed in the process.

The colorations obtained are especially resistant

to atmospheric attack and to chemical agents including, in particular, light, washing and permanent-waving.

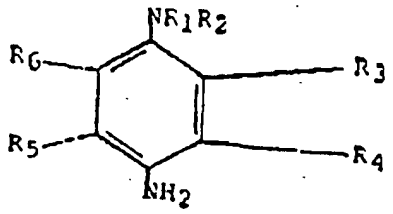
A subject of the invention hence consists of a process for dyeing keratinous fibres employing an oxidation base and an iodide in the same composition.

Another subject of the invention consists of compositions intended for use for the dyeing of keratinous fibres, containing an oxidation base and an iodide.

The subject of the invention is also multi-component dyeing kits or outfits employing the compositions used in the different stages of the dyeing process.

Other subjects of the invention will become apparent on reading the description and examples which follow.

The process for dyeing keratinous fibres, preferably human, according to the invention, is essentially characterized in that at least one composition (A) is applied on these fibres, this composition (A) containing, in a medium suitable for dyeing, at least one oxidation base, chosen from para-phenylenediamines, corresponding to the formula (I):



(I)

in which:

R_1 and R_2, which may be identical or different, can denote hydrogen, a C_1-C_6 lower alkyl group, a C_1-C_6 alkyl radical substituted with one or more hydroxy group(s) or with a methoxy, methylsulphonylamino or aminocarbonyl group, a furfuryl group, or a phenyl radical optionally substituted with an amino group; R_3 and R_6 can denote, independently of one another, hydrogen, a C_1-C_6 lower alkoxy group, a halogen atom such as a chlorine atom, a C_1-C_6 lower alkyl group, or a C_1-C_6 lower alkyl group substituted with one or more hydroxy group(s); and R_4 and R_5 denote, independently of one another, hydrogen, a C_1-C_6 lower alkoxy group, a C_1-C_6 lower alkyl group, or a halogen atom such as chlorine, it not being possible for R_1 and R_2 simultaneously to denote hydrogen when R_3, R_4, R_5 and R_6 all denote hydrogen; as well as their salts with inorganic or organic acids, N,N'-diphenylalkylenediamines in which the phenyl groups are substituted at the para position with an OH or amino group optionally substituted with a C_1-C_6 alkyl group, it being possible for the amino groups joined by the alkylene group to be substituted with C_1-C_6 alkyl,

C_1-C_6 hydroxyalkyl or C_1-C_6 aminoalkyl, para-aminophenols, ortho-aminophenols, ortho-phenylenediamines and heterocyclic oxidation bases, in combination with iodide ions, the application of this composition (A) being preceded or followed by the application of a composition (B) which contains, in a medium suitable for dyeing, hydrogen peroxide at a pH of between 2 and 12, and preferably between 2 and 7, and especially between 2 and 5.

The application of the compositions (A) and (B) is optionally separated by a rinsing.

In the process according to the invention, the iodide ion is preferably an alkali metal, alkaline earth metal or ammonium iodide, and especially potassium iodide.

Among especially preferred compounds of the formula (I), there may be mentioned 2-methyl-para-phenylenediamine, 2-methoxy-para-phenylenediamine, 2-chloro-N-methyl-para-phenylenediamine, N-furfuryl-para-phenylenediamine, 3-methoxy-N^1-methyl-paraphenylenediamine, 2-chloro-para-phenylenediamine, N-methyl-para-phenylenediamine, 2,3-dimethyl-para-phenylenediamine, 5-chloro-N^1-methyl-p-phenylenediamine, 5-methyl-N^1,N^1,-dimethyl-p-phenylenediamine, 5-methyl-N^1-ethyl-N^1-(aminocarbonylmethyl)-p-phenylenediamine, 5-methyl-N^1-ethyl-N^1-(methylsulphonylaminoethyl)-p-phenylenediamine, N-(2-methoxyethyl)-p-phenylenediamine, 2,6-dimethyl-p-phenylenediamine, N,N-bis(2-hydroxyethyl)-p-phenylenediamine. The N,N'-diphenylalkylenediamines include, for example N,N'-bis-(2-hydroxyethyl)-N,N'-bis(p-aminophenyl)ethylenediamine.

Their salts with acids such as the monohydrochlorides, dihydrochlorides or sulphates are also suitable.

Among p-aminophenols which are more especially usable according to the invention, there may be mentioned p-aminophenol, 2-methyl-p-aminophenol, 2,3-dimethyl-p-aminophenol, 2,6-dimethyl-p-aminophenol, 3-methoxy-p-aminophenol, 2-chloro-p-aminophenol, N-methyl-p-aminophenol and 3-(methylthio)-p-aminophenol, of which 2-methyl-p-aminophenol is preferred.

Among ortho bases, ortho-aminophenol, 5-chloro-ortho-aminophenol and ortho-phenylenediamine are chosen more especially according to the invention.

Among heterocyclic bases, it is preferable, according to the invention, to use 2,3-diamino-6-methoxypyridine and 2-(2-hydroxyethyl)amino-5-aminopyridine and their salts, and still more especially 3,6-diaminopyridine, 2,6-dimethoxy-3-aminopyridine and 2-methylamino-3-amino-6-methoxypyridine.

More especially preferred oxidation bases are 2-methyl-p-phenylenediamine, N-(2-methoxyethyl)-p-phenylenediamine, N,N-bis(2-hydroxyethyl)-p-phenylenediamine and 2-methyl-p-aminophenol.

These different oxidation bases can be used mixed or alone, in combination with iodide ions.

A subject of the invention hence consists of a process as defined above, in which the compositi n (A)

contains exclusively an oxidation base as defined above, with iodide ions, without the presence of other compounds capable of reacting with them, for the purpose of forming a dye by coupling.

An embodiment of the invention consists in using, in combination with the oxidation base(s) 5,6-dihydroxyindole, preferably present in proportions of between 0.01 and 5% by weight, and preferably between 0.03 and 3% by weight, relative to the weight of the composition (A).

The subject of the invention is also dyeing compositions intended for use in a process for dyeing keratinous fibres, especially human hair, comprising at least one oxidation base defined above and iodide ions, in a medium suitable for dyeing. The oxidation bases used in the compositions according to the invention are preferably chosen from the preferred dyes defined above.

The composition (A), containing the oxidation base and iodide ions, generally contains the base in proportions of between 0.01 and 10% by weight relative to the total weight of the composition (A), and preferably between 0.25 and 5% by weight. The proportion of iodide in these same compositions is preferably between 0.007 and 4% by weight expressed as I^- ions, and preferably between 0.08 and 1.5% by weight expressed as I^- ions, relative to the total weight of the composition (A).

The hydrogen peroxide content used in the compositions (B) is generally between 1 and 40 volumes, and preferably between 2 and 20 volumes, and more especially between 3 and 10 volumes.

The ratio of the oxidation base to the iodide ions is preferably between 0.05 and 10, and more especially between 0.5 and 2.

The process according to the invention is carried out by arranging exposure times, for the different compositions applied in each of the different stages of the process, of between 10 seconds and 45 minutes, and preferably of the order of 2 to 25 minutes, and more especially of the order of 2 to 10 minutes.

The Applicant found, in effect, that the process according to the invention made it possible to obtain colorations that were both rapid and strong, penetrating well into the fibres, and in particular human keratinous fibres such as hair, without degrading the hair shaft. These colorations also possess good resistance to washing and to light and are odourless.

He was also able to note that hair dyed several times, following regrowth, by means of the processes and the compositions employed, according to the invention, was softer and shinier and had good mechanical properties, compared with hair dyed employing the processes and compositions of the prior art.

By means of the process and the compositions

according to the invention, relatively intense colorations are obtained in relatively short times, of the order of 5 to 15 minutes.

The compositions used for carrying out the process according to the invention can be presented in various forms, such as more or less thickened or gelled liquids, creams, emulsions and foams, or other forms suitable for carrying out dyeing.

The dyeing compositions intended for use in the process according to the invention, and containing the oxidation base in combination with iodide ions, generally contain an aqueous medium consisting of water and/or a water/solvent(s) mixture, the solvent(s) preferably being chosen from organic solvents such as ethyl alcohol, propyl or isopropyl alcohol, tert-butyl alcohol, ethylene glycol, ethylene glycol monomethyl, monoethyl and monobutyl ethers, ethylene glycol monoethyl ether acetate, propylene glycol, propylene glycol monomethyl ether and dipropylene glycol monomethyl ether, and methyl lactate. The especially preferred solvents are ethyl alcohol and propylene glycol.

The oxidation bases can also be stored with the iodides in a medium consisting of anhydrous solvents, this composition being mixed at the time of use with an aqueous medium.

When the medium is aqueous, the composition (A) has a pH of between 2 and 7, and preferably between 3.5 and 7.

According to the invention, an anhydrous solvent denotes a solvent comprising less than 1% of water.

When the medium consists of a water/solvent(s) mixture, the solvents are present in concentrations preferably of between 0.5 and 75% by weight relative to the total weight of the composition, and especially between 2 and 50%, and more especially between 2 and 20%.

The compositions according to the invention can contain other adjuvants customarily used in the dyeing of keratinous fibres.

In the preferred application to the dyeing of hair, these compositions can contain, in particular, fatty amides in proportions of 0.5 to 10%, anionic, cationic, nonionic or amphoteric surfactants, or mixtures thereof, present in proportions of between 0.1 and 50% by weight, thickening agents, perfumes, sequestering agents, film-forming agents, treatment agents, dispersants, conditioners, preservatives, opacifiers, and agents that swell keratinous fibres.

The thickeners may be chosen more especially from sodium alginate, gum arabic, guar gum, biopolymers such as xanthan gum or scleroglucans, cellulose derivatives such as methylcellulose, hydroxyethylcellulose, hydroxypropylmethylcellulose, carboxymethylcellulose sodium salt and acrylic acid polymers. It is also possible to use inorganic thickening agents such as bentonite. These thickeners, used alone or mixed, are preferably present in

proportions of between 0.1 and 5% by weight relative to the total weight of the composition, and advantageously between 0.5 and 3%.

The acidifying agents which are usable in the preferred embodiment of the process, employing the compositions at acid pH, may be chosen from lactic acid, acetic acid, tartaric acid, phosphoric acid, hydrochloric acid and citric acid.

It is also possible to adjust the pH with alkalinizing agents chosen, in particular, from amines such as alkanolamines and alkylamines, and alkali metal or ammonium hydroxides or cabonates, in particular when the precursors are used in the form of salts of strong acids.

When the composition is used in the form of a foam, it may be packaged under pressure in an aerosol device, in the presence of a propellant and at least one foam generator. The foam generating agents can be anionic, cationic, nonionic or amphoteric foaming polymers, or surfactants of the type defined above.

For the purpose of carrying out the process according to the invention, the different compositons may be packaged in a multi-compartment device also referred to as a kit or outfit for dyeing, comprising all the components intended for application for a single dyeing on keratinous fibres, in successive applications with or without premixing. Such devices are known per se, and can comprise a first compartment containing the composition (A), containing

the oxidation base in the presence of iodide ions in a medium suitable for dyeing, and, in a second compartment, a hydrogen peroxide solution.

When the medium containing the oxidation base and the iodide ions is an anhydrous medium, it is mixed, before use, with the aqueous vehicle suitable for dyeing, optionally present in a third compartment.

The composition containing the oxidation base and iodide ions in an anhydrous medium can optionally be applied directly on wet keratinous fibres.

When the medium suitable for dyeing is aqueous, the composition in the first compartment preferably possesses a pH of between 2 and 7, and especially between 3.5 and 7. The pH of the composition containing hydrogen peroxide is between 2 and 12, but is is preferably acid and between 2 and 7, and more especially between 2 and 5.

The multi-compartment devices which are usable according to the invention can be equipped with means, known per se, for mixing at the time of use, and can be packaged under an inert atmosphere.

The process and the compositions used according to the invention can be employed for dyeing hair which is natural or has already been dyed, permanent-waved or otherwise, or straightened, or hair which has been strongly or lightly bleached and optionally permanent-waved. It is also possible to use them for dyeing furs or wool.

The examples which follow are designed to illustrate

the invention, without a limitation of the latter being implied.

EXAMPLE 1

The dyeing of natural, 90% white hair, was carried out by successive applications, and without rinsing between the two applications, of a dyeing solution A, of the following composition:

3-methoxy-1-N-methyl-p-phenylenediamine dihydrochloride	1.00 g
potassium iodide	0.1 g
ethyl alcohol	5.00 g
water	qs 100 g
triethanolamine qs pH = 6	

After 5 minutes of contact, a solution B) of 12.5 volumes H_2O_2 (pH 3.7) was then applied for 5 minutes. The hair was rinsed with water. After drying, a bluish dark ash blonde coloration was obtained.

EXAMPLE 2

Dyeing of permed, 90% white hair was carried out by successive applications, without rinsing between the two applications, of a dye A) of the following composition:

2-methyl-p-phenylenediamine dihydrochloride	1.95 g
potassium iodide	0.1 g
ethyl alcohol	5.00 g
water	qs 100 g
triethanolamine qs pH = 6	

After 5 minutes of contact, a solution B) of

12.5 volumes H_2O_2 (pH 3.7) was then applied for 5 minutes. The hair was rinsed with water. After drying, a pearlescent light chestnut colour was obtained.

EXAMPLE 3

Dyeing of permed, 90% white hair was carried out by successive application, and without rinsing between the two applications, of a dyeing solution A) of the following composition:

N-furfuryl-p-phenylenediamine dihydrochloride	2.6 g
potassium iodide	1.00 g
ethyl alcohol	5.00 g
water	qs 100
triethanolamine qs pH = 6	

After 5 minutes of contact, a solution B) of 12.5 volumes H_2O_2 (pH 3.7) was applied for 5 minutes. The hair was rinsed with water. After drying, a slightly coppery chestnut colour was obtained.

EXAMPLE 4

Example 3 was repeated using an amount of potassium iodide of 0.1 g in the dyeing solution A). A light chestnut colour was obtained.

EXAMPLE 5

Dyeing of natural, 90% white hair was carried out by applying successively, and without rinsing between the two applications, a dyeing solution A) of the following composition:

N-methyl-p-phenylenediamine	1.95 g
potassium iodide	0.1 g
ethyl alcohol	5.00 g
water	qs 100 g

triethanolamine qs pH = 6

After 5 minutes of contact, a solution of 5 volumes H_2O_2 (pH 3.9) was applied for 5 minutes. The hair was rinsed with water. After drying, a bluish medium grey colour was obtained.

EXAMPLE 6

Dyeing of natural, 90% white hair was carried out by applying successively, and without rinsing between the two applications, a dyeing solution A) of the following composition:

N-methyl-p-phenylenediamine	1.95 g
potassium iodide	0.1 g
ethyl alcohol	5.00 g
water	qs 100 g

triethanolamine qs pH = 6

After 5 minutes of contact, a solution B) of 12.5 volumes H_2O_2 (pH 3.7) was applied for 5 minutes. The hair was rinsed with water. After drying, a golden chestnut colour was obtained.

EXAMPLE 7

Dyeing of natural, 90% white hair was carried out by successive applications and without rinsing between the two applications, of a dyeing solution A) of the

following composition:

N-methyl-2-chloro-p-phenylene-diamine sulphate	1.3 g
Potassium iodide	0.1 g
Ethyleneglycol monobutyl ether	20.00 g
Water	qs 100 g

Triethanolamine qs pH = 6

After 5 minutes of contact, a solution B) of 12.5 volumes H_2O_2 (pH 3.7) was applied for 5 minutes. The hair was rinsed with water. After drying, a natural blond colour was obtained.

EXAMPLE 8

Dyeing of permed, 90% white hair was carried out by successive applications and without rinsing between the two applications, of a dyeing solution A) of the following composition:

2-methoxy-p-phenylenediamine dihydrochloride	2.11 g
Potassium iodide	0.1 g
Ethyl alcohol	5.00 g
Water	qs 100

Triethanolamine qs pH = 6

After 5 minutes of contact, a solution B) of 12.5 volumes H_2O_2 (pH 3.7) was applied for 5 minutes. The hair was rinsed with water. After drying, a dark grey coloration with glints of steel was obtained.

EXAMPLE 9

Dyeing of natural 90% white hair was carried out by successive applications, and without rinsing between the two applications, of the following dyeing composition A):

2-chloro-p-phenylene-diamine sulphate	2.00 g
Ammonium iodide	1.00 g
Ethyl alcohol	10.00 g
Xanthane gum, sold under the trade name RHODOPOL 23 SC by the company RHONE POULENC	1.00 g
Glycoside alkyl ether sold at the concentration of 60% AS under the trade name TRITON CG 110 by the company SEPPIC	5.00 g AS
Water	qs 100 g

Triethanolamine qs pH = 6.2

After 5 minutes of contact, the hair was towel-dried and then a 12.5 volumes hydrogen peroxide solution (pH 3.7) was applied while massaging the scalp for 5 minutes. After rinsing the hair with water, a natural coppery chestnut colour was obtained.

EXAMPLE 10

Dyeing of natural, 90% white hair was carried out by successive applications, and without rinsing between the two applications, of a solution B) of 10 volumes hydrogen peroxide which was left in contact for

5 minutes. The hair was then towel dried and the following dyeing composition A) was applied:

N-furfuryl-p-phenylene-diamine dihydrochloride	3.00 g
Sodium iodide	1.5 g
Ethyl alcohol	10.00 g
Xanthane gum sold under the name RHODOPOL SC 23 by the company RHONE-POULENC	1.00 g
Glycoside alkyl ether sold at the concentration of 60% AS under the trade name TRITON CG 110 by the company SEPPIC	5.00 g AS
Water	qs 100 g
Triethanolamine qs pH = 6	

The scalp was massaged for 5 minutes. The hair was rinsed with water and a blond coloration with glints of grey green was obtained.

EXAMPLE 11

Dyeing of natural, 90% white hair was carried out by successive applications, and without rinsing between the two applications, of a solution B) of 5 volumes hydrogen peroxide (pH 3.9) which was left in contact for 5 minutes. The hair was then towel dried and the following dyeing composition A) was applied:

2-methyl-p-phenylenediamine dihydrochloride	3.00 g

Sodium iodide	1.00 g
Ethyl alcohol	10.00 g
Xanthane gum sold under the trade name RHODOPOL SC 23 by the company RHONE-POULENC	1.00 g
Glycoside alkyl ether sold at the concentration of 60% AS under the trade name TRITON CG 110 by the company SEPPIC	5.00 g AS
Water	qs 100
Triethanolamine qs pH = 6	

The scalp was massaged for 5 minutes. The hair was rinsed with water and a natural medium grey colour was obtained.

EXAMPLE 12

Dyeing of natural, 90% white hair was carried out, by successive applications and with rinsing between the two applications, of a dyeing solution A) of the following composition:

2,3-dimethyl-p-phenylenediamine dihydrochloride	2.1 g
Potassium iodide	0.1 g
Ethyl alcohol	5.00 g
Water	qs 100 g
Triethanolamine qs pH = 6	

After 5 minutes of contact and subsequent rinsing, an aqueous solution B) of 12.5 volumes H_2O_2

(pH 3.7) was applied for 5 minutes. The hair was rinsed with water. After drying, an iridescent light ash blonde colour was obtained.

EXAMPLE 13

Dyeing of natural, 90% white hair was carried out by successive application of 2 compositions A) and B) with rinsing in between.

Dyeing composition (A):

N,N-bis(2-hydroxyethyl) -p-phenylenediamine sulphate	1.9 g	
Potassium iodide	0.7 g	
Ethyl alcohol	5.0 g	
Xanthane gum sold under the trade name RHODOPOL SC 23 by the company RHONE-POULENC	2.0 g	
Glycoside alkyl ether sold at the concentration of 60% AS under the trade name TRITON CG 110 by the company SEPPIC	2.1 g AS	
Triethanolamine qs pH = 6.5		
Preservative	qs	
Water	qs 100	g

Composition (B):

Aqueous solution of 20 volumes hydrogen peroxide	50.0 g
Ethyl alcohol	5.0 g

Triethanolamine qs pH = 4

Water qs 100 g

The composition (A) was left in contact for 10 minutes. The hair was rinsed with water and then composition (B) was applied and left to act for 10 minutes. After rinsing and drying, a light brownish grey colour was obtained.

EXAMPLE 14

Dyeing of natural, 90% white hair was carried out, by successive application of two compositions (A) and (B) with rinsing in between.

Dyeing composition (A):

2-methyl-p-phenylenediamine dihydrochloride	1.26 g
Potassium iodide	0.7 g
Ethyl alcohol	5.0 g
Xanthane gum sold under the trade name RHODOPOL SC 23 by the company RHONE-POULENC	2.0 g
Glycoside alkyl ether sold at the concentration of 60% AS under the trade name TRITON CG 110 by the company SEPPIC	2.1 g AS
Triethanolamine qs pH = 6.5	
Preservative	qs
Water	qs 100 g

Composition (B):

Aqueous solution of 20 volumes hydrogen peroxide	50.0 g
Ethyl alcohol	5.0 g
Triethanolamine qs pH=4	
Water	qs 100 g

The composition (A) was left in contact for 10 minutes. The hair was rinsed with water and then the composition (B) was applied and left to act for 10 minutes. After rinsing and drying, a dark golden blond colour was obtained.

EXAMPLE 15

Dyeing of natural, 90% white hair was carried out by successive application of two compositions (A) and (B) with rinsing in between.

Dyeing composition (A):

N-(2-methoxyethyl)-p-phenylenediamine dihydrochloride	1.65 g
Potassium iodide	0.7 g
Ethyl alcohol	5.0 g
Xanthane gum sold under the trade name RHODOPOL SC 23 by the company RHONE-POULENC	2.0 g
Glycoside alkyl ether sold at the concentration of 60% AS under the trade name TRITON CG 110 by the company SEPPIC	2.1 g AS

Triethanolamine qs pH = 6.5	
Preservative	qs
Water	qs 100 g

Composition (B):

Aqueous solution of 20 volumes hydrogen peroxide	50.0 g
Ethyl alcohol	5.0 g
Triethanolamine qs pH = 4	
Water	qs 100 g

Composition (A) was left in contact for 10 minutes. The hair was rinsed with water and then composition (B) was applied and left to act for 10 minutes. After rinsing and drying, a medium grey-beige colour was obtained.

EXAMPLE 16

Dyeing of natural, 90% white hair was carried out by successive application of two corpositions (A) and (B) with rinsing in between.

Dyeing composition (A):

2-methyl-p-aminophenol	0.4 g
Potassium iodide	0.35 g
Ethyl alcohol	10.0 g
Xanthane gum sold under the trade name RHODOPOL SC 23 by the company RHONE-POULENC	2.0 g
Glycoside alkyl ether sold at the concentration of 60% AS under	

the trade name TRITON CG 110 by the company SEPPIC	2.1 g AS
Citric acid qs pH = 6.5	
Preservative	qs
Water	qs 100 g

Composition (B):

Aqueous solution of 20 volumes hydrogen peroxide	50.0 g
Ethyl alcohol	10.0 g
Triethanolamine qs pH = 4	
Water	qs 100 g

Composition (A) was left in contact for 10 minutes. The hair was rinsed with water and then composition (B) was applied and left to act for 10 minutes. After rinsing and drying, a beige-golden blond colour was obtained.

EXAMPLE 17

Dyeing of natural, 90% white hair was carried out by successive application of two compositions (A) and (B) with rinsing in between.

Dyeing composition (A):

o-aminophenol	0.35 g
Potassium iodide	0.35 g
Ethyl alcohol	10.0 g
Xanthane gum sold under the trade name RHODOPOL SC 23 by the company RHONE-POULENC	2.0 g

Glycoside alkyl ether sold at the concentration of 60% AS under the trade name TRITON CG 110 by the company SEPPIC	2.1 g AS
Triethanolamine qs pH = 6.5	
Preservative	qs
Water	qs 100 g

Composition (B):

Aqueous solution of 20 volumes hydrogen peroxide	50.0 g
Ethyl alcohol	10.0 g
Triethanolamine qs pH = 4	
water	qs 100 g

Composition (A) was left to act for 10 minutes. The hair was rinsed with water and then composition (B) was applied and left to act for 10 minutes. After rinsing and drying, an intense coppery-golden colour was obtained.

EXAMPLE 18

Dyeing of natural permed, 90% white hair was carried out by applying in a first step the following composition:

N,N-bis(2-hydroxyethyl)-p-phenylenediamine sulphate	1.0 g
Potassium iodide	1.0 g
Ethyl alcohol	10.0 g
Xanthane gum sold under the	

trade name RHODOPOL SC 23 by the company RHONE-POULENC	2.0 g
Glycoside alkyl ether sold under the trade name TRITON CG 110 by the company SEPPIC	2.1 g AS
Triethanolamine qs pH = 6	
Water	qs 100 g

The composition was left in contact for 15 minutes. The hair was rinsed with water and then an aqueous solution of 20 volumes hydrogen peroxide was applied for 5 minutes, the pH having been adjusted to 8 with triethanolamine. After rinsing and drying, an intense golden blond was obtained on the hair.

EXAMPLE 19

N,N-bis(2-hydroxyethyl)-p-phenylenediamine sulphate	1.0 g
5,6-dihydroxyindole	0.2 g
Potassium iodide	1.0 g
Ethyl alcohol	10.0 g
Xanthane gum sold under the trade name RHODOPOL SC 23 by the company RHONE-POULENC	2.0 g
Glycoside alkyl ether sold under the trade name TRITON CG 110 by the company SEPPIC	2.1 g AS
Triethanolamine qs pH = 6	
Water	qs 100 g

This composition was applied for 15 minutes on natural, 90% white hair. The hair was rinsed with water and then an aqueous solution of 20 volumes hydrogen peroxide, of pH 3, was applied for 5 minutes.

After another rinse followed by drying, a slightly pearlescent medium grey was obtained.

EXAMPLE 20

Dyeing of natural permed, 90% white hair was carried out by successive application of two compositions (A) and (B).

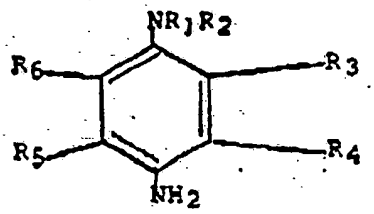
Dyeing composition (A):

3,6-diaminopyridine dihydrochloride	1.8 g
Ethyl alcohol	5.0 g
Potassium iodide	1.0 g
Triethanolamine qs pH = 6	
Preservative	qs
Water	qs 100 g

Composition (A) was applied to the hair and left in contact for 5 minutes. Then, without rinsing, a composition (B) was applied: aqueous solution of 12.5 volumes hydrogen peroxide at pH 3.7, which was left to act for 5 minutes. After rinsing with water and drying, the hair was dyed a mahogany chestnut.

CLAIMS

1. A process for dyeing keratinous fibres which comprises applying to the fibres, in any order, at least one composition containing, in a medium suitable for dyeing, at least one oxidation base which is a para-phenylenediamine of the formula (I):



(I)

in which:

R_1 and R_2, which may be identical or different, denote hydrogen, a C_1-C_6 alkyl group, a C_1-C_6 alkyl radical substituted with one or more hydroxy groups or with one or more methoxy, methylsulphonylamino, aminocarbonyl, or furfuryl groups, or phenyl radicals optionally substituted with an amino group; R_3 and R_6 denote, independently of one another, hydrogen, a C_1-C_6 alkoxy group, a halogen atom, a C_1-C_6 alkyl group, or a C_1-C_6 alkyl group substituted with one or more hydroxy groups; and R_4 and R_5 denote, independently of one another, hydrogen, a C_1-C_6 alkoxy group, a C_1-C_6 alkyl group or a halogen atom with the proviso that, when R_3, R_4, R_5 and R_6 are simultaneously hydrogen R_1 and R_2 are not both hydrogen; a salt thereof, with an inorganic or organic acid; or is an N,N'-diphenylalkylenediamine in which the

phenyl groups are substituted at the para position by OH or an amino group optionally substituted with a C_1-C_6 alkyl group, it being possible for the amino groups joined by the alkylene group to be substituted with C_1-C_6 alkyl, C_1-C_6 hydroxyalkyl or C_1-C_6 aminoalkyl; a para-aminophenol, ortho-aminophenol, ortho-phenylenediamine or a heterocyclic oxidation base, in combination with iodide ions, and a composition (B) which contains, in a medium suitable for dyeing, hydrogen peroxide at a pH of from 2 to 12.

2. A process according to claim 1, in which the composition (B) is at a pH of from 2 to 7.

3. A process according to claim 2 in which the pH is from 2 to 5.

4. A process according to any one of the preceding claims in which the iodide ions are from alkali metal, alkaline earth metal or ammonium iodides.

5. A process according to any one of the preceding claims which comprises applying to the fibres, in a first stage, the composition (A) comprising, in a medium suitable for dyeing, iodide ions in the form of an alkali metal, alkaline earth metal or ammonium iodide, and at least one oxidation base as defined in claim 1; and, in a second stage, the composition (B) containing, in a medium suitable for dyeing, hydrogen peroxide.

6. A process according to any one of the preceding claims in which the aqueous composition (B) is "1

to 40 volumes" hydrogen peroxide.

7. A process according to claim 6 in which the aqueous composition is "2 to 20 volumes" hydrogen peroxide.

8. A process according to any one of the preceding claims in which the different compositions are applied for 10 seconds to 45 minutes.

9. A process according to claim 8 in which the compositions are applied for 2 to 10 minutes.

10. A process according to any one of the preceding claims in which the oxidation base is a compound of formula (I) which is 2-methyl-para-phenylenediamine, 2-methoxy-para-phenylenediamine, N-methyl-2-chloro-para-phenylenediamine, N-furfuryl-para-phenylenediamine, 3-methoxy-N^1-methyl-paraphenylenediamine, 2-chloro-para-phenylenediamine, N-methyl-para-phenylenediamine, 2,3-dimethyl-para-phenylenediamine, 5-chloro-N^1-methyl-p-phenylenediamine, 5-methyl-N^1,N^1-dimethyl-p-phenylenediamine, 5-methyl-N^1-ethyl-N^1-(aminocarbonylmethyl)-p-phenylenediamine, 5-methyl-N^1-ethyl-N^1-(methylsulphonylaminoethyl)-p-phenylenediamine, N-(2-methoxyethyl)-p-phenylenediamine, 2,6-dimethyl-p-phenylenediamine, N,N-bis(2-hydroxyethyl)-p-phenylenediamine or, as an N,N'-diphenylalkylenediamine, N,N'-bis-(2-hydroxyethyl)-N,N'-bis(p-aminophenyl)ethylenediamine; or a salt thereof with inorganic or organic acids.

11. A process according to any one of claims 1

to 9, in which the oxidation base is p-aminophenol, 2-methyl-p-aminophenol, 2,3-dimethyl-p-aminophenol, 2,6-dimethyl-p-aminophenol, 3-methoxy-p-aminophenol, 2-chloro-p-aminophenol, N-methyl-p-aminophenol or 3-(methylthio)-p-aminophenol.

12. A process according to any one of claims 1 to 9, in which the oxidation base is ortho-aminophenol, 5-chloro-ortho-aminophenol or ortho-phenylenediamine.

13. A process according to any one of claims 1 to 9, in which the oxidation base is a heterocyclic base which is 2,3-diamino-6-methoxypyridine, 2-(2-hydroxyethyl)-amino-5-aminopyridine, 3,6-diaminopyridine, 2,6-dimethoxy-3-aminopyridine or 2-methylamino-3-amino-6-methoxypyridine.

14. A process according to any one of the preceding claims in which composition (A) also contains 5,6-dihydroxyindole.

15. A process according to any one of the preceding claims in which the oxidation base present in the composition (A) is 2-methyl-p-phenylenediamine, N-(2-methoxyethyl)-p-phenylenediamine, N,N-bis(2-hydroxy-ethyl)-p-phenylenediamine or 2-methyl-p-aminophenol.

16. A process according to any one of the preceding claims in which the medium is water or a water/solvent mixture, having a pH of from 2 to 7.

17. A process according to claim 16 in which the pH is from 3.5 to 7.

18. A process according to any one of claims 1 to 15 in which the medium is an anhydrous solvent.

19. A process according to any one of claims 16 to 18 in which the solvent is ethyl alcohol, propyl or isopropyl alcohol, tert-butyl alcohol, ethylene glycol, ethylene glycol monomethyl, monoethyl or monobutyl ether, ethylene glycol monoethyl ether acetate, propylene glycol, propylene glycol monomethyl ether or dipropylene glycol monomethyl ether; or methyl lactate.

20. A process according to any one of the preceding claims in which the compositions comprise at least one adjuvant which is a fatty amide in a proportion of 0.05 to 10%; an anionic, cationic, nonionic or amphoteric surfactant, or a mixture thereof, present in a proportion of from 0.1 to 50% by weight; a thickening agent in a proportion of from 0.1 to 5% by weight; a perfume, sequestering agent, film-forming agent, treatment agent, dispersant, conditioner, preservative, opacifier or an agent that swells keratinous fibres.

21. A process according to claim 1 and substantially as hereinbefore described in any one of Examples 1 to 20.

22. A process according to any one of claims 1 to 21 in which the keratinous fibres are human hair.

23. A dyeing composition for keratinous fibres, which comprises at least one oxidation base as defined in

claim 1 in combination with iodide ions.

24. A composition according to claim 23 in which the oxidation base is as defined in any one of claims 10 to 13.

25. A composition according to claim 23 or 24 which also contains 5,6-dihydroxyindole.

26. A composition according to any one of claims 23 to 25 in which the oxidation base is present in a proportion of from 0.01 to 10% by weight.

27. A composition according to claim 26 in which the proportion of oxidation base is 0.25 to 5% by weight.

28. A composition according to any one of claims 23 to 27 in which the proportion of iodide is from 0.007 to 4% by weight expressed as I^- ions relative to the total weight of the composition.

29. A composition according to claim 28 in which the proportion of iodide is 0.08 to 1.5%.

30. A composition according to any one of claims 23 to 29 in which the ratio by weight of oxidation base to iodide is from 0.005:1 to 10:1.

31. A composition according to claim 30 in which the ratio is from 0.5:1 to 2:1.

32. A composition according to claim 23 and substantially as hereinbefore described in any one of Examples 1 to 20.

33. A multi-compartment device or kit for dyeing

which comprises, in a first compartment, a composition (A) according to any one of claims 23 to 32 in a medium suitable for dyeing and, in a second compartment, an aqueous composition of hydrogen peroxide.

34. A device according to claim 33 in which the medium suitable for dyeing in the first compartment is aqueous, and possesses a pH of from 2 to 7.

35. A device according to claim 34 in which the pH is from 3.5 to 7.

36. A device according to any one of claims 33 to 35 in which the aqueous composition of hydrogen peroxide has a pH of from 2 to 12.

37. A device according to claim 36 in which the pH is from 2 to 7.

38. A multi-compartment device or kit for dyeing keratinous fibres which comprises a first compartment containing a composition containing, in an anhydrous solvent medium, iodide ions and at least one oxidation base as defined in any one of claims 1, or 10 to 13; a second compartment containing an aqueous medium suitable for dyeing; and a third compartment containing an aqueous composition of 1 to 40 volumes hydrogen peroxide at a pH of from 2 to 12, the composition present in the second compartment being designed to be mixed with the contents of the first compartment at the time of use.

39. A multi-compartment device or kit according to claim 38 in which the pH in the third compartment is from 2 to 7.

Published 1988 at The Patent Office, State House, 66 71 High Holborn, London WC1R 4TP. Further copies may be obtained from The Patent Office, Sales Branch, St Mary Cray, Orpington, Kent BR5 3RD. Printed by Multiplex techniques ltd, St Mary Cray, Kent, Con. 1/87.